(19) Europäisches Patentamt
European Patent Office
Offic européen des brevets

(11) Publication number: 0 489 179 A1

(12) # EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC

(21) Application number: 91911946.1

(22) Date of filing: 26.06.91

(86) International application number: PCT/JP91/00861

(87) International publication number: WO 92/00601 (09.01.92 92/02)

(51) Int. Cl.5: H01L 21/302

(30) Priority: 27.06.90 JP 171791/90

(43) Date of publication of application: 10.06.92 Bulletin 92/24

(84) Designated Contracting States: DE FR GB

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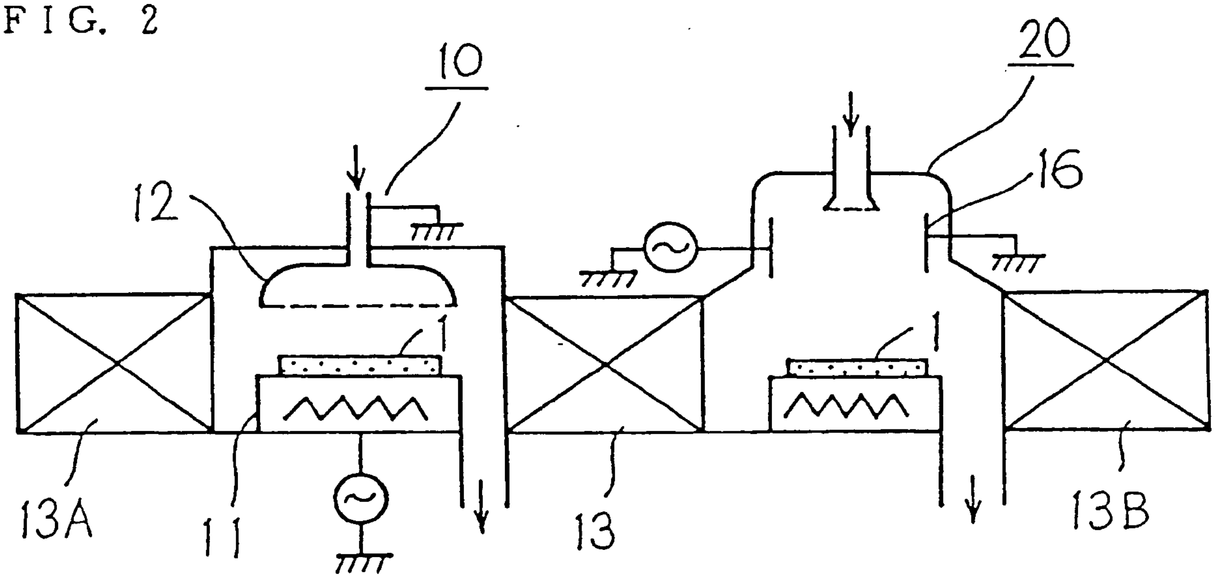
(54) # METHOD OF MANUFACTURING SEMICONDUCTOR INTEGRATED CIRCUIT AND EQUIPMENT FOR THE MANUFACTURE.

(57) In order to prevent after-corrosion of the wiring and electrodes which are formed by patterning a thin film (2) of aluminum or an alloy thereof through the use of a reactive ion etching (RIE) that uses an etchant including chlorine gas or a gaseous chloride, chlorine molecules remained on the surfaces of the wirings and the electrodes are removed by exposing the wiring and the electrodes directly to a plasma generated in atmosphere including steam or to a neutral active species extracted from the plasma. This processing is performed in the ashing for removing a resist mask (3) used in the RIE by adding steam to an atmosphere including oxygen, or is performed independently after the ashing. In order to performing the latter independent processing, in an automatic processing system disclosed, an ashing equipment (20) is connected with a RIE equipment (10) through an evacuatable load-lock chamber (13), and an aftertreatment equipment (40) for removing residual chlorine is connected with the ashing equipment (20) through a second load-lock chamber (13c).

EP 0 489 179 A1

FIG. 2



BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a lithography process for use during the production of semiconductor integrated circuits. More particularly, it relates to the removal of chlorine or bromine which remains on a surface of a conductive film when the conductive film made of aluminum or an alloy thereof is dry-etched by using chlorine or bromine, or an alloy thereof as an etchant.

Description of the Related Art

For a wiring forming a semiconductor integrated circuit formed on a substrate, such as silicon wafer or the like, thin films of aluminum (Al) or thin films of an alloy in which silicon (Si) or copper (Co) is added into aluminum are often used. To prevent an increase in the contact resistance of an aluminum or aluminum alloy thin film wiring due to an alloy reaction with a silicon wafer, a so-called barrier metal of a thin film of titanium (Ti), titanium nitride (TiN), or titanium-tungsten (TiW) is provided between the silicon wafer and the aluminum thin film.

Patterning of an aluminum or aluminum alloy film for such wiring as described above is performed generally by a lithography in which the conductive film is selectively etched by using a mask formed of a resist layer. Anisotropic etching is required to make it possible to form fine wiring patterns. At the present time, reactive ion etching (RIE) is a typical anisotropic etching method. For removing a resist mask, a so-called ashing, which can be performed without using a solvent, such as trichloro ethylene which poses a problem relating to the environmental pollution, is used.

The above-mentioned etching and ashing methods are both a dry process. So, they are suitable for process control or automatic processing and free from the contamination due to impurities in an etching solution or a solvent as in a wet process. An outline of these processes will now be explained with reference to Figs. 1 and 2.

Figs. 1(a), 1(b), and 1(c) show a change in the cross section of a member to be processed in the above-described dry etching and ashing processes. Fig. 2 schematically shows an example of the construction of a processing system for automatically performing the etching and ashing operations.

In the system in Fig. 2, a RIE apparatus 10 for etching aluminum films and an ashing apparatus 20 for removing resist masks after etching are connected to each other via a load lock chamber 13 which is capable of a vacuum. Aluminum films are transported by the load lock chamber 13 from the RIE apparatus 10 to the ashing apparatus 20 without contacting the atmosphere. Another load lock chamber 13A is disposed on the entry side of the RIE apparatus 10, and another load lock chamber 13B is disposed on the exit side of the ashing apparatus 20. Substrates on which aluminum films are formed can be inserted into or taken out of the RIE apparatus 10 and the ashing apparatus 20 without introducing air into the apparatuses 10 and 20 by the load lock chambers 13A and 13B.

Referring to Fig. 1(a), for example, an aluminum film 2 is deposited on the whole of a surface of a substrate 1 composed of a silicon wafer, following which a resist is applied onto the aluminum film 2. By applying ultra-violet rays, electron beams, or an energy beam, such as excimer laser, or the like, to a predetermined position of this resist and then developing, a mask 3 composed of the aforesaid resist is formed. The surface of the substrate 1 on which the aluminum film 2 is formed is generally covered with an unillustrated insulation layer composed of SiO_2, etc. The surface of the substrate 1 or a lower layer wiring is exposed inside a contact hole provided on a part of the insulation layer.

The substrate 1 with the mask 3 formed thereon as described above is placed on a stage 11 inside the RIE apparatus 10 through the load lock chamber 13A in Fig. 2. Then, for example, chlorine gas (Cl_2) is introduced into the RIE apparatus 10 and, while the inside of such apparatus is being maintained at a predetermined pressure, a plasma is generated by applying a voltage between the stage 11 and an electrode 12. As a result, the aluminum film 2 is anisotropically etched, as shown in Fig. 1(b).

The substrate 1 having the aluminum film 2 etched as described above is transported to the ashing apparatus 20 through the load lock chamber 13 in Fig. 2. Then, for example, an oxygen gas (O_2) is introduced into the ashing apparatus 20, and while the inside of such apparatus is being maintained at a predetermined pressure, a voltage is applied between a pair of electrodes 16 which are opposed to each other. As a result, a plasma is generated between the electrodes 16. The mask 3 composed of the aforesaid resist reacts mainly with oxygen atoms or molecules, or ions in this plasma and vaporizes, being exhausted outside the ashing apparatus 20. In this manner, the mask 3 on the aluminum film 2 is removed, as shown in Fig. 1(c).

Shown in Fig. 2 is the ashing apparatus 20 which performs plasma ashing in which a member to be processed is directly exposed to the plasma. The above-described processes are performed in the same manner as for an automatic processing system equipped with a so-called down-flow type ashing apparatus which exposes the member to be processed to only neutral active species extracted from a plasma. As a means for generating the aforesaid plasma, an excitation by microwaves radiation or an excitation using a high-frequency induction coil is often used in place of the electrode 16.

In a RIE for films of aluminum or an alloy thereof, gaseous chlorine compound, such as boron trichloride (BCl_3) or silicon tetrachloride ($SiCl_4$), bromine gas (Br_2), or gaseous bromine compound, such as hydrogen bromide (HBr) or boron tribromine (BBr_3), are also used as an etchant.

If the substrate 1 upon which etching and ashing has been performed as described above is taken out into the atmosphere, a phenomenon is often recognized in that "after-corrosion" occurs in wiring composed of thin films of aluminum or an alloy of aluminum. The resistance of the wiring increases due to this after-corrosion, and in extreme cases disconnection occurs. Such after-corrosion proceeds while a semiconductor integrated circuit in a state in which the wiring is covered with a passivation insulation layer is used for a long period of time, thereby resulting in the poor reliability of products.

The mechanism causing such after-corrosion as described above is not yet completely clarified. It is considered that after-corrosion is due to the fact that chlorine, bromine, or their compounds, which are components of the etchant used in etching, remains on the surface of an aluminum film. That is, the residual chlorine, for example, reacts with the water of the atmosphere, generating hydrochloric acid (HCl), etc., which causes an aluminum film to become corroded.

The introduction of the automatic processing system shown in Fig. 2 enables an aluminum film to be sent to an ashing apparatus without contacting the atmosphere. And, since most of the remaining chlorine or the like are removed by the ashing apparatus. Accordingly, after-corrosion described above is considerably reduced.

In recent years, however, aluminum-copper (Al-Cu) alloys, in which electro-migration and stress migration do not often occur in comparison with pure aluminum films, have come to be used as a wiring material. As mentioned earlier, thin films of Ti, TiN, or TiW are used as barrier metals for blocking the alloy reaction between a silicon substrate or polycrystal silicon lower-layer wiring, and aluminum wiring.

The use of Al-Cu alloy films or barrier metals promotes after-corrosion because an electric cell is formed on the grain boundaries of different types of metals or the interface of the barrier metal and aluminum films because of the presence of hydrochloric acid generated from the above-mentioned residual chlorine. Therefore, even if the automatic processing system shown in Fig. 2 is introduced, a problem is posed in that after-corrosion cannot be completely avoided.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide an apparatus for preventing after-corrosion in wiring composed of the aforesaid thin films of aluminum or an alloy thereof, more particularly, to provide a method which is capable of more completely removing chlorine or the like which remains after the aforesaid ashing on all the exposed surfaces including the side of the wiring and on the surface of a substrate exposed in the periphery of the wiring, and to provide an apparatus for performing such a method.

As a result, the present invention improves the production yield of semiconductor integrated circuits having wiring composed of thin films of aluminum or an alloy thereof, and enhances the reliability of the semiconductor integrated circuits for use for a long period of time.

The present invention is characterized by including any one of the following modes. That is,

(1) As shown in Fig. 3(a), a film 2 of aluminum or an alloy thereof formed on a surface of a substrate 1 is covered with a mask 3 composed of a resist. The aluminum film 2 is exposed through the mask 3 and selectively etched by using chlorine, bromine, or a gaseous etchant containing a compound thereof. The mask 3, used in the aforesaid etching, is ashed and removed, when it is directly exposed to a plasma generated in an atmosphere containing oxygen and water vapor, or exposed to neutral active species extracted from the plasma. Residual chlorine, bromine, or a compound thereof on the surface of the film 2 which is exposed as a result of the removal of the mask 3 is dissociated from the surface by forming volatile compounds, such as HCl, and removed. Or,

(2) While the mask 3 is ashed by neutral active species extracted from a plasma generated in the atmosphere containing oxygen gas, the film 2, which is revealed along the removal of the mask 3 is exposed to a plasma generated in an atmosphere containing water vapor, in order that residual chlorine or the like is removed as described in above (1). Or,

(3) As shown in Fig. 3(b), after removing the mask 3 by an ashing process, the thin film 2 is exposed

directly to a plasma generated in an atmosphere containing water vapor or to neutral active species extracted from the plasma in order that residual chlorine or the like on the surface thereof is removed as described in above (1).

In Figs. 3(a) and 3(b), O_2 and H_2O are shown as representative of the aforesaid neutral active species, CO_2 as representatives of the reaction products when the resist mask 3 is removed, and HCl as representative of the product when the aforesaid neutral active species and the residual chlorine react and are removed. Of course, the aforesaid neutral active species and the products are not limited to these examples.

(4) An automatic processing system is constructed in order that the removal of residual chlorine or the like in the mode (3) above, can be performed by using an apparatus different from an ashing apparatus. That is, as shown in Fig. 4, a after-treatment apparatus 40 is connected, via a load lock chamber 13C, to the ashing apparatus 20, which is connected to the RIE apparatus 10 via the load lock chamber 13. For the after-treatment apparatus 40, either a down flow type or a plasma processing type where a member to be processed is directly exposed to the plasma, is used in the same manner as in the ashing apparatus 20.

In Fig. 4, reference numeral 1 denotes a substrate having a thin film of aluminum or an alloy thereof selectively covered with a resist mask but not etched. Reference numeral 1' denotes a substrate on which the aforesaid thin film is etched. Reference numeral 1" denotes a substrate from which the aforesaid resist mask has been removed.

The applicant of the present invention has proposed an ashing method whereby water is added into the aforesaid gas for the purpose of increasing the ashing speed in down-stream ashing in which gases having oxygen are used (Japanese Patent Laid-Open No. 64-48421, Application date: August 19, 1987). In this method, however, conditions for etching (a process anterior to an ashing operation) are not specified. Moreover, in this application, there is not even a suggestion that the addition of water to the ashing atmosphere prevents after-corrosion of aluminum films which are patterned by using an etchant, such as chlorine gas or the like.

The applicant of the present invention has also proposed a method of preventing after-corrosion by exposing aluminum films which are etched by using a chlorine-type reactive gas, to water vapor in a pressure-reduced atmosphere (Japanese Patent Laid-Open No. 3-41728, Application date: July 7, 1989). In this method, however, the removal of residual components, such as chlorine or the like, which cause after-corrosion, depends on a thermal reaction, and a substrate to be processed is heated to approximately 120°C in order to promote this reaction.

In the present invention in contrast with these applications, aluminum films patterned by using an etchant, such as chlorine gas or the like is exposed directly to a plasma generated in an atmosphere containing water vapor or to active species extracted from this plasma, such as H_2O in an excited state or hydrogen (H) in an atomic state, or OH free radicals, or the like, in order for residual chlorine or the like to be removed. As a consequence, since a removal reaction is more actively promoted than in a method which exposes aluminum films simply to water vapor as in the above-described application, it is possible to remove chlorine or the like which is strongly attached and cannot be removed by a thermal reaction.

These and other objects, features and advantages of the present invention will become clear when reference is made to the following description of the preferred embodiments of the present invention, together with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view showing a process for patterning wiring of a semiconductor integrated circuit;

Fig. 2 is a schematic view showing an example of the construction of an automatic processing apparatus for performing wiring patterning in a semiconductor integrate circuit;

Fig. 3 is a schematic cross-sectional view showing a principle of the present invention;

Fig. 4 is a schematic view showing an example of the construction of an automatic processing apparatus of the present invention;

Fig. 5(a) is a schematic view showing an example of the construction of an automatic processing apparatus used for effecting the present invention;

Fig. 5(b) is a schematic view showing a detailed construction of an ashing apparatus 20 or an after-treatment apparatus 40 in Fig. 4 or Fig. 5(a);

Fig. 6 is a schematic sectional view showing an example of wiring construction processed by a method of the present invention;

Fig. 7 is a schematic view showing a detailed construction of an example of the substitute ashing apparatus 20 or the after-treatment apparatus 40 in Fig. 4 or Fig. 5(a);
Fig. 8 is a schematic view showing a detailed construction of an example of the substitute ashing apparatus 20 in Fig. 4 or Fig. 5(a); and
Fig. 9 is a graph showing an effect of reducing the amount of residual chlorine according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Various embodiments of the present invention will be explained below with reference to the accompanying drawings. Throughout the figures, the same parts as those in figures shown previously are given the same reference numerals.

(First Embodiment)

A substrate 1 on which is formed a mask 3 composed of a resist, with which a film 2 composed of aluminum containing 2% copper (Al-2%Cu) is selectively covered, as shown in Fig. 1(a), is transported into a RIE apparatus 10 through a load lock chamber 13A in the automatic processing system shown in Fig. 2 and placed on a stage 11.

After the inside of the RIE apparatus 10 is turned to a vacuum of, for example, 2 x 10^{-4} Torr, a gaseous mixture of chlorine gas (Cl_2) and silicon tetrachloride ($SiCl_4$) is introduced thereto. The total pressure is maintained at 8 x 10^{-2} Torr, and a high-frequency voltage is applied between the stage 11 and the electrode 12. As a result, the aluminum film 2 (not shown) on the substrate 1 is anisotropically etched by ions and radicals in the plasma generated between the stage 11 and the electrode 12.

The substrate 1 with the aluminum film 2 etched as described above is transported to the ashing apparatus 20 through the load lock chamber 13 which has been turned into a vacuum and placed on a stage 14. The ashing apparatus 20 in the figure is of a so-called plasma ashing type. Oxygen gas (O_2) and water vapor (H_2O) are introduced into the ashing apparatus 20 each at a flow rate of 1 to 2 SLM, and 100 to 300 SCCM, and the total pressure is maintained at 1 Torr. Then, the substrate 1 is heated, for example, to 100 to 200° C, by a heater disposed on the stage 14. In this state, plasma is generated by supplying, for example, high frequency power of approximately 1.5 kW at a frequency of 2.54 GHz; and the aforesaid resist mask 3 is ashed. Even when the aluminum film 2 processed as in the above-described embodiment was left in the air for 48 hours, an occurrence of after-corrosion could not be detected. In comparison, an ashing operation was performed without adding water vapor to gas introduced to an ashing chamber 21B in the above-described embodiment, then it was detected that after-corrosion occurred when the aluminum film 2 was left in the air for one hour.

Also, the same results as described above were obtained in cases where chlorine (Cl_2) gas introduced into the RIE apparatus 10 in the above description was substituted by bromine (Br_2) gas, and silicon tetrachloride ($SiCl_4$) was substituted by silicon tetrabromide ($SiBr_4$).

(Second Embodiment)

Etching and ashing operations were performed on the aluminum film 2 and the resist mask 3 in the same manner as in the above-described embodiment. The aluminum film 2, composed of Al-2%Cu, is formed on the substrate 1 via a barrier metal 4 (made of a titanium (Ti) film 4A and a titanium nitride (TiN) film) as shown in Fig. 6. In that operation, no occurrence of after-corrosion could be detected even when the aluminum film 2 from which the mask 3 was removed was left in the air for 48 hours.

(Third Embodiment)

An aluminum film was etched and ashed by using an automatic processing system shown in Fig. 5(a). The RIE apparatus 10 in the figure is of a parallel flat-plate electrode type having the stage 11 on which a substrate to be processed is placed and an electrode 12 opposing the stage 11. The ashing apparatus 20 is of a so-called down flow type and has a detailed construction, for example, as shown in Fig. 5(b). In this example, a cylindrical chamber 21 made of aluminum is divided into a plasma generation chamber 21A and an ashing chamber 21B by a shower head 28 in which a large number of small openings having a diameter of approximately 2 to 3 mm are disposed. A microwave generation source 23 like a magnetron is connected to one end of the plasma generation chamber 21A via a microwave transmission window 27.

Referring to Figs. 5(a) and 5(b), the substrate 1 made of a silicon wafer having a diameter of 4 inches in which a film made of Al-2%Cu is formed is transported into the RIE apparatus 10 through the load lock chamber 13A, placed on the stage 11, and heated to a predetermined temperature. A gaseous mixture of BCl_3, $SiCl_4$, and Cl_2 was introduced, as an etchant, into the RIE apparatus 10, and the total pressure was maintained at 0.08 Torr. For this reason, the flow rate of BCl_3, $SiCl_4$, and Cl_2 was respectively controlled at 80 SCCM, 400 SCCM, and 10 SCCM. In this state, a plasma is generated by supplying high-frequency power between the stage 11 and the electrode 12. The power supplied at this time is 350W. The aforesaid aluminum film is anisotropically etched for approximately 180 seconds under these conditions.

Next, the substrate 1 is transported, via the load lock chamber 13, into the ashing apparatus 20, placed on the stage 14, and heated to 180°C by a heater 24 disposed on the stage 14. Oxygen (O_2) and water vapor (H_2O) are mixed at the rate of the flow rate of 1350 SCCM and 150 SCCM, respectively, and introduced into the plasma generation chamber 21A via a gas introduction pipe 25. The total pressure is maintained at 1.0 Torr. In this state, the microwave generation source 23 is activated to generate a plasma. The output of the microwave generation source 23 at this time is 1.0 kW, and the operating time is 120 seconds. The resist mask is ashed and residual chlorine (Cl) on the aluminum film are removed by neutral active species in the plasma generated in this manner.

That is, a shower head 28 is composed of, for example, pure aluminum. Therefore, no plasma will occur inside the ashing chamber 21B, whereas only the neutral active species inside the plasma generation chamber 21A flow out into the ashing chamber 21B through small openings of the shower head 28. These neutral active species include atomic oxygen (O), hydrogen (H), excited molecules of O_2, H_2O, etc., and active species, such as OH free radicals. It is considered that each of these is involved with the ashing of a resist mask, but it is considered that the ashing is contributed mainly by atomic oxygen (O) and excited oxygen molecules (O_2).

On the other hand, the residual chlorine on the surface of the aluminum film etched as described above reacts mainly with atomic hydrogen (H) and OH free radicals in the aforesaid neutral active species to produce a volatile compound, for instance, hydrogen chloride (HCl). The residual chlorine is released from the substrate 1, and discharged to the outside through an exhaust pipe 26. Residual chlorine present on the SiO_2 surface exposed in the periphery of the aluminum film 2 similarly produces HCl and is discharged.

According to a downflow type apparatus, the degradation of characteristics of elements forming an integrated circuit is small because the substrate 1 to be processed is not subjected to ion bombardment, as in a plasma ashing type apparatus shown in Fig. 2. Also, chances that impure ions of sodium (Na), heavy metals, etc. are injected are reduced.

An occurrence of after-corrosion was not detected even when an aluminum film processed as in the above-described embodiment was left in the air for 48 hours.

(Fourth Embodiment)

An operation for etching an aluminum film composed of Al-2%Cu, an operation for ashing a resist mask, and an after-treatment for removing residual chlorine were performed by using the automatic processing system shown in Fig. 4 in which the after-treatment apparatus 40 for removing residual chlorine or bromine on the surface of an aluminum film is disposed independently of the ashing apparatus 20 for removing a resist mask. Since the after-treatment apparatus 40 is of a down-flow type apparatus shown in Fig. 5(b) similarly to the ashing apparatus 20, the same reference numerals are used to explain the details thereof.

The substrate 1, on which are formed the aluminum film 2 composed of Al-2%Cu shown in Fig. 1(a) and the mask 3 formed of a resist with which the aluminum film 2 is covered, is etched by the RIE apparatus 10 in the automatic processing system shown in Fig. 4. The etching conditions are the same as those for the above-described embodiments.

Next, the substrate 1 is transported into the ashing apparatus 20 through the load lock chamber 13, placed on the stage 14, and heated to 180°C by the heater 24 disposed on the stage 14. Oxygen (O_2) is introduced into the plasma generation chamber 21A via the gas introduction pipe 25 at a flow rate of 1350 SCCM, and the total pressure is maintained at 1.0 Torr. In this state, the microwave generation source 23 is activated to generate a plasma. The output of the microwave generation source 23 at this time is 1.0 kW, and the operating time is 120 seconds. The resist mask is ashed by neutral active species in the plasma generated in this manner.

Next, the substrate 1 is transported, via the load lock chamber 13C, into the after-treatment chamber 40, placed on the stage 16, and heated to 180°C by a heater disposed on the stage 16. Water vapor (H_2O) is introduced into the plasma generation chamber 21A via the gas introduction pipe 25 at a flow rate of 150 SCCM, and the total pressure is maintained at 1.0 Torr. In this state, the microwave generation source 23 is

activated to generate a plasma. The output of the microwave generation source 23 at this time is 1.0 kW. The residual chlorine (Cl) on the aluminum film is exhausted, as HCl, to the outside of the after-treatment apparatus 40 by neutral active species in the plasma generated in this manner.

No occurrence of after-corrosion was detected even when each of the three kinds of aluminum films on the substrate 1 was left in the air for 48 hours, upon which aluminum films after-treatment was performed for different times (30, 90, and 180 seconds) under the above-described conditions.

(Fifth Embodiment)

In comparison, samples of ① to ⑬ shown in Table 1 were produced. The amount of residual chlorine were measured, and the occurrence of after-corrosion when these samples were left in the air for 48 hours was observed. These samples are formed of Al-2%Cu thin films formed on a silicon wafer having a diameter of 4 inches. Conditions for treating each sample in Table 1 are as follows. That is,

①: A state in which a resist mask is left on the aluminum film, with reactive ion etching being performed in the same manner as in the above-described embodiments 1 through 4.

②: Downflow ashing by using a plasma generated in oxygen (O_2) is performed upon a resist mask on an aluminum film on which reactive ion etching is performed in the same manner as in the above-described embodiments 1 through 4 (Flow rate of O_2: 1500 SCCM, pressure: 1 Torr, microwaves power: 1.0 kW, substrate temperature: 180° C, and ashing time: 180 seconds).

③: Downflow ashing is performed upon a resist mask on an aluminum film on which reactive ion etching is performed in the same manner as in the above-described embodiments 1 through 4 by a plasma generated in mixed gas of oxygen (O_2) and carbon tetrafluoride (CF_4) (Flow rate of O_2: 1500 SCCM, flow rate of CF_4: 150 SCCM pressure: 1 Torr, microwaves power: 1.0 kW, substrate temperature: 180° C, and ashing time: 120 seconds).

④: Corresponds to the above-described third embodiment.

⑤ to ⑦: After downflow ashing is performed upon samples by a plasma generated in the oxygen (O_2) in the same manner as in the above ②, the samples were exposed to water vapor (H_2O) (Flow rate of H_2O: 1500 SCCM, pressure: 1 Torr, substrate temperature: 180° C, and ashing times: 30, 90, and 180 seconds).

⑧ to ⑩ : Corresponds to the above-described fourth embodiment.

⑪ to ⑬ : After downflow ashing is performed upon samples by a plasma generated in the oxygen (O_2) in the same manner as for the sample of ② above, they were after-treated by the down flow of plasma generated in hydrogen (H_2) (Flow rate of H_2: 1500 SCCM, pressure: 1 Torr, microwaves power: 1.5 kW, substrate temperature: 180° C, and ashing times: 30, 90, and 180 seconds).

Fig. 9 is a graph schematically showing the relationships between the amount of residual chlorine and the conditions for treatment shown in Table 1. Graphic symbols indicating each sample in Fig. 9 are given in Table 1 in order for facilitating cross-reference.

As can be seen from Table 1 and Fig. 9, the amount of residual chlorine is considerably low in the third embodiment (④ in Table 1 and ◊ in Fig. 9) and in the fourth embodiment (⑧ and ⑩ in Table 1 and △ in Fig. 9) of the present invention, in the former, an ashing operation being performed by using a plasma generated in a gaseous mixture in which water vapor (H_2O) was added into oxygen (O_2) and,in the latter, after-treatment being performed by using a plasma of water vapor (H_2O) after an ashing operation. Also, after-corrosion does not practically occur in the embodiments. In contrast, an effect for reducing the amount of residual chlorine is small in an ashing operation using the other gases or after-treatment posterior to the ashing operation, and thus after-corrosion cannot be completely prevented.

In the third embodiment, the automatic processing system of Fig. 5(a) for performing an ashing operation and removing residual chlorine concurrently was used. In the fourth embodiment, the automatic processing system which is capable of performing after-treatment for removing residual chlorine separately from the ashing operation was used. Advantages and disadvantages of these automatic processing system will now be compared.

The automatic processing system of Fig. 5(a) can perform an ashing operation and remove residual chlorine simultaneously, so it is efficient. When an ashing operation and the removal of residual chlorine are performed separately, these processes can be performed by using the same apparatus. Therefore, the present invention has an advantage in that the processing system is simple in construction. However, as will be described later, when water vapor must be removed from the ashing apparatus, it takes a long period of time for baking of the chamber 21 and vacuum exhaust.

In contrast, the automatic processing system of Fig. 4 can avoid the influences of water vapor on an ashing operation. Particularly, in an ashing operation using gas in which carbon tetrafluoride (CF_4) is added

into oxygen (O_2), if there is water vapor (H_2O) in this gas atmosphere, CF_4 is consumed by the reaction of $CF_4 + 2H_2O \rightarrow 4HF + CO_2$, with the result that the ashing speed becomes lower. In such a case, therefore, the automatic processing system of Fig. 4 is effective.

The ashing apparatus 20 in Fig. 5(a) and Fig. 4 and the after-treatment apparatus 40 in Fig. 4 can be substituted by one constructed as shown in Fig. 7 or 8.

Shown in Fig. 7 is a so-called plasma ashing type apparatus by which the substrate 1 to be processed is directly exposed to a plasma generated between electrodes 32. In Fig. 7, reference numeral 31 denotes a chamber, and reference numeral 33 denotes a high-frequency power supply.

Fig. 8 shows an apparatus which is basically the same as the so-called downflow type shown in Fig. 5-(b). It is characterized in that oxygen (O_2) and water vapor (H_2O) can be introduced separately to the ashing apparatus 20, as in the third embodiment. That is, only oxygen (O_2) is introduced into the plasma generation chamber 21A, and water vapor (H_2O) is introduced into the ashing chamber 21B. Another microwave generation source 36 is disposed in the midsection of the gas introduction pipe 35 for that purpose.

Neutral active species generated in the plasma generation chamber 21A flow into the ashing chamber 21B after passing through the small openings of the shower head 28. Meanwhile, plasma of water vapor (H_2O) is generated by the microwave generation source 36. Ions therein recombines with electrons while passing through the gas introduction pipe 35. Therefore, excited H_2O molecules, neutral atomic hydrogen (H) and oxygen (O), or OH free radicals are introduced into the ashing chamber 21B.

Many different embodiments of the present invention may be constructed without departing from the spirit and scope of the present invention. It should be understood that the present invention is not limited to the specific embodiments described in this specification, and is only limited in the appended claims.

Table 1

Conditions	Amount of residual chlorine μm g/cm^2	10^{15}atoms/cm^2	After-corrosion	Symbols shown in Fig. 9
① Etching only	0.92±0.06	16.0±1.0	Large	○
② Downflow ashing using O_2 after ①	0.89±0.06	15.5±1.0	Large	●
③ Downflow ashing using O_2+CF_4 after ①	0.54±0.03	9.3±0.4	Small	■
④ Downflow ashing using O_2+H_2O after ①	0.23±0.03	4.0±0.5	No	◇
⑤ Exposure to H_2O after ② (30sec)	0.51±0.02	8.7±0.3	Small	▲
⑥ Exposure to H_2O after ② (90sec)	0.48±0.01	8.1±0.2	Small	▲
⑦ Exposure to H_2O after ② (180sec)	0.45±0.04	7.6±0.7	Small	▲
⑧ Downflow treatment using H_2O after ② (30sec)	0.28±0.01	4.7±0.2	None	△
⑨ Downflow treatment using H_2O after ② (90sec)	0.15±0.00	2.5±0.0	No	△
⑩ Downflow treatment using H_2O after ② (180sec)	0.11±0.01	1.9±0.1	No	△
⑪ Downflow treatment using H_2 after ② (30sec)	0.68±0.01	11.8±0.2	Small	▼
⑫ Downflow treatment using H_2O after ② (90sec)	0.68±0.01	11.7±0.1	Small	▼
⑬ Downflow treatment using H_2 after ② (180sec)	0.64±0.01	11.1±0.2	Small	▼

Exposure to H_2O: heated at 120°C in water vapor at 0.1 Torr.

Claims

1. A method for producing semiconductor integrated circuits, comprising the steps of:

   a first step of selectively etching a metallic film formed on a surface of a substrate and exposed through a mask by using a gaseous etchant containing chlorine, bromine, or a compound thereof after the metallic film is selectively covered with the mask made of a resist; and

   a second step of removing the mask used in said etching by ashing it by using a plasma generated in an atmosphere containing oxygen gas and water vapor, and removing chlorine, bromine, or a compound thereof, which are components of said gaseous etchant which remains on the surface of said metallic film exposed as a result of the removal of said mask, by forcing it to be released from said substrate.

2. The method according to claim 1, wherein said metallic film is composed of aluminum or an alloy thereof.

3. The method according to claim 2, wherein a barrier layer for blocking a reaction between said metallic film and said substrate is provided between the metallic film and the substrate.

4. The method according to claim 1, wherein said substrate is maintained at a temperature of between 100° and 250°C in said second step.

5. The method according to claim 1, wherein, in said second step, said mask and said metallic film exposed as the result of the removal of said mask are exposed to neutral active species extracted from said plasma.

6. The method according to claim 1, wherein, in said second step, said mask and said metallic film exposed as the result of the removal of said mask are exposed to said plasma.

7. A method for producing semiconductor integrated circuits, comprising the steps of:
   a first step of selectively etching a metallic film formed on a surface of a substrate and exposed through a mask by using a gaseous etchant containing chlorine, bromine, or a compound thereof after the metallic film is selectively covered with the mask made of a resist; and
   a second step of removing the mask used in said etching by ashing it by exposing it to neutral active species extracted from the plasma generated in the first atmosphere, after a plasma is generated separately in both a first atmosphere containing oxygen gas and a second atmosphere containing water vapor, and removing chlorine, bromine, or a compound thereof, which are components of said residual etchant on the surface of said metallic film exposed as the result of the removal of said mask by exposing it to at least neutral active species in the plasma generated in the second atmosphere and by forcing it to be released from said substrate.

8. The method according to claim 7, wherein said metallic film is composed of aluminum or an alloy thereof.

9. The method according to claim 8, wherein a barrier layer for blocking the reaction between said metallic film and said substrate is provided between the metallic film and the substrate.

10. The method according to claim 7, wherein said substrate is maintained at a temperature of between 100° and 250°C in said second step.

11. A method for producing semiconductor integrated circuits, comprising the steps of:
   a first step of selectively etching a metallic film exposed through a mask by using a gaseous etchant containing chlorine, bromine, or a compound thereof after the metallic film formed on a surface of a substrate is selectively covered with the mask made of a resist; and
   a second step of removing the mask used in said etching by ashing it by using a first plasma generated in an atmosphere containing oxygen gas; and
   a third step of removing chlorine, bromine, or a compound thereof, which are components of said residual etchant on the surface of said metallic film exposed as the result of the removal of said mask by forcing it to be released from said substrate by using a second plasma generated in an atmosphere containing water vapor.

12. The method according to claim 11, wherein said second and third processes are performed by using the same apparatus.

13. The method according to claim 11, wherein said second and third processes are performed by using a different apparatus for each process.

14. The method according to claim 13, wherein the apparatus used in said third process is of a downflow type.

15. The method according to claim 11, wherein said metallic film is composed of aluminum or an alloy

thereof.

16. The method according to claim 11, wherein a barrier layer for blocking the reaction between said metallic film and said substrate is provided between the metallic film and the substrate.

17. The method according to claim 11, wherein said substrate is maintained at a temperature of between 100° and 250°C in said second step.

18. The method according to claim 11, wherein said metallic film is exposed to neutral active species extracted from the second plasma in the third process.

19. The method according to claim 11, wherein said metallic film is exposed to said second plasma in the third process.

20. An apparatus for producing semiconductor integrated circuits, comprising:
an etching chamber for selectively etching a metallic film formed on a substrate and covered with a mask formed of a resist by using a gaseous etchant containing chlorine, bromine, or a compound thereof;
an ashing chamber for ashing said mask formed on said substrate and connected, through a first load lock chamber which is capable of making a vacuum, to said etching chamber and sent from said etching chamber by using a plasma generated in an atmosphere containing oxygen gas so as to remove it; and
an after-treatment chamber for removing residual chlorine, bromine, or a compound thereof on the surface of said metallic film on said substrate connected to said etching chamber through a first load lock chamber which is capable of making a vacuum and sent from said etching chamber by using a plasma generated in an atmosphere containing water vapor.

21. The apparatus according to claim 20, wherein said after-treatment chamber comprises:
a plasma generating section into which gas containing water vapor is introduced and into which a plasma generating means for generating a plasma in said gas is connected; and
a treatment section which is connected to said plasma generating section, these said sections being divided from each other by a division wall in which small openings through which neutral active species in a plasma pass are provided, and in which said substrate is placed.

22. The apparatus according to claim 20, wherein gas containing water vapor is introduced into said after-treatment chamber, said substrate is placed therein, and said after-treatment chamber has parallel flat-plate type electrodes disposed on both sides of said substrate with said substrate as a center thereof.

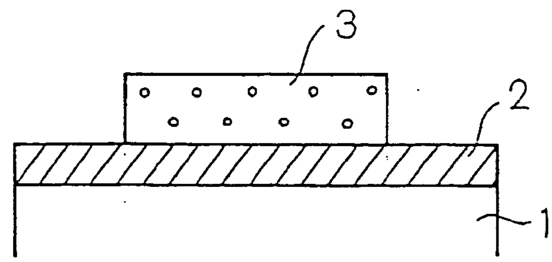


FIG. 1 (a)

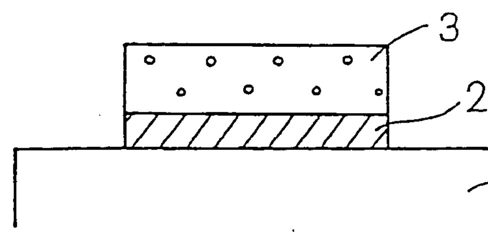


FIG. 1 (b)

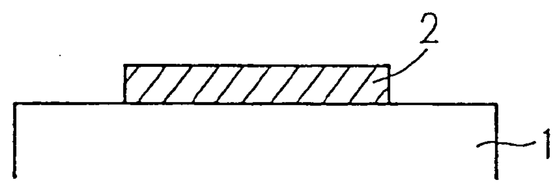
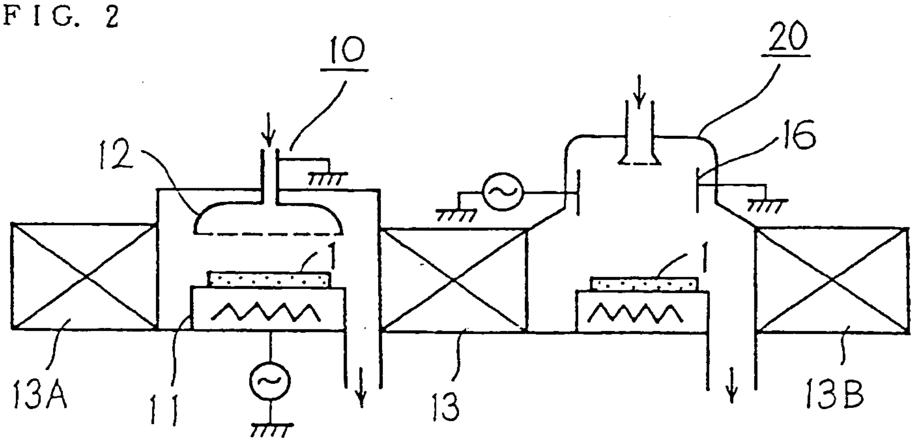
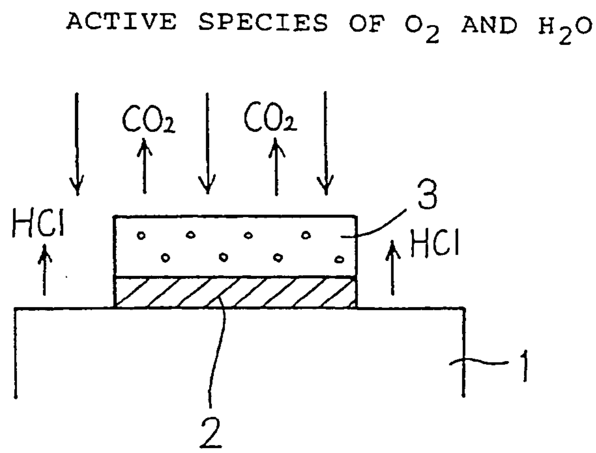


FIG. 1 (c)

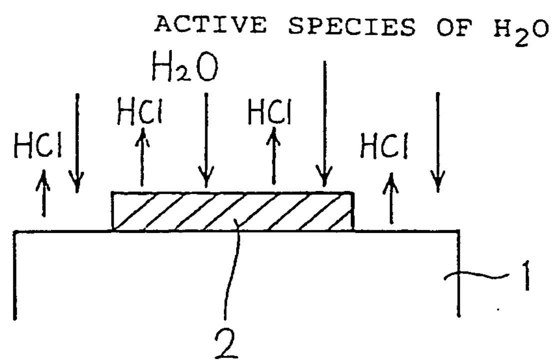
FIG. 2



F I G. 3 (a)



F I G. 3 (b)



F I G. 4

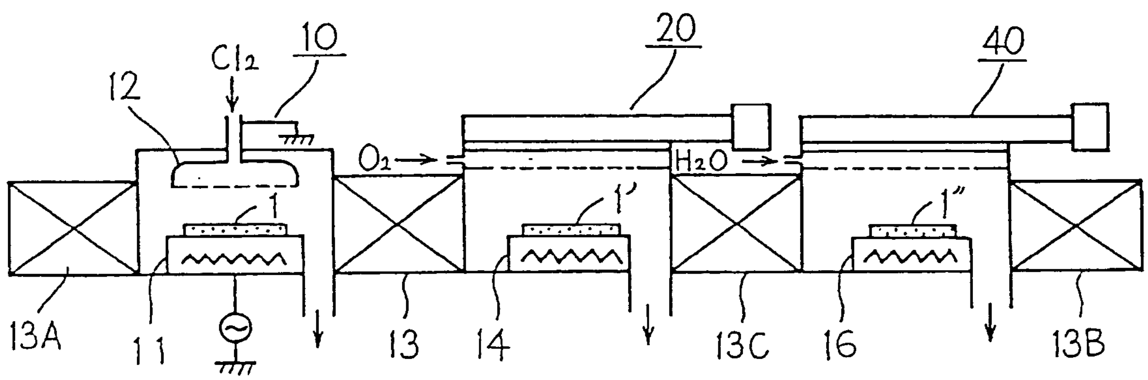


FIG. 5 (a)

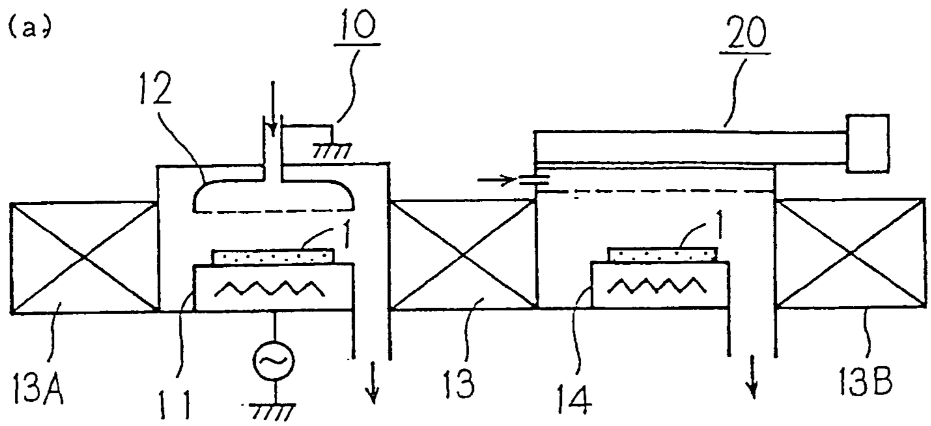
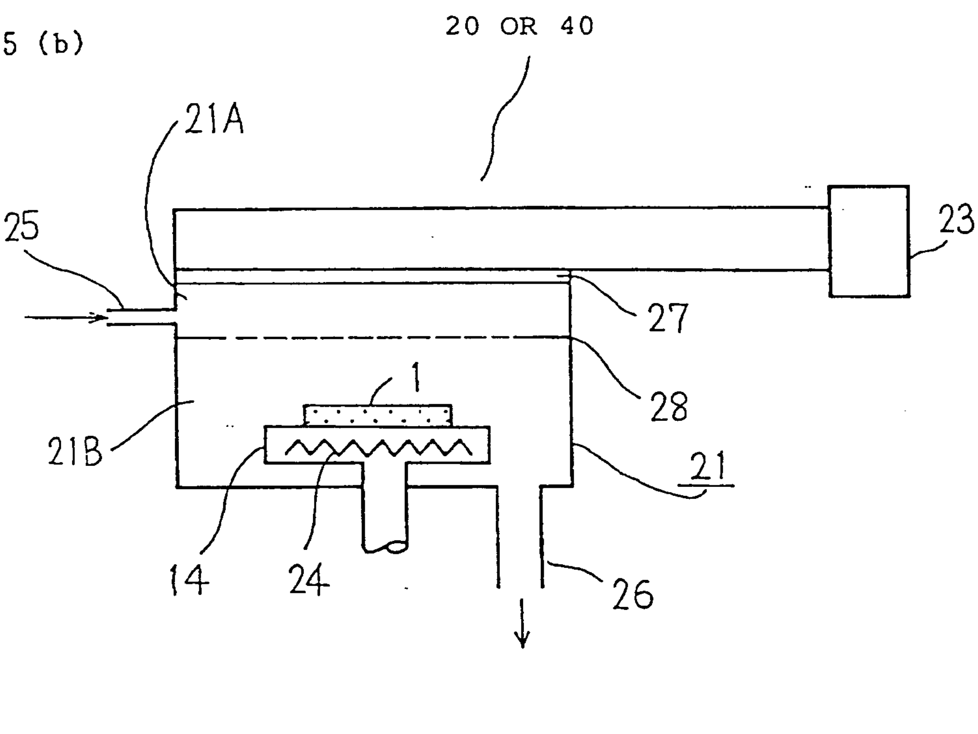
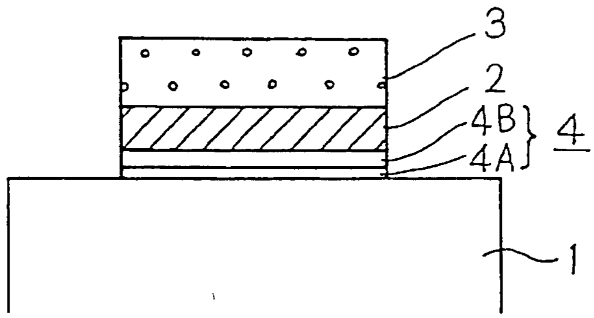


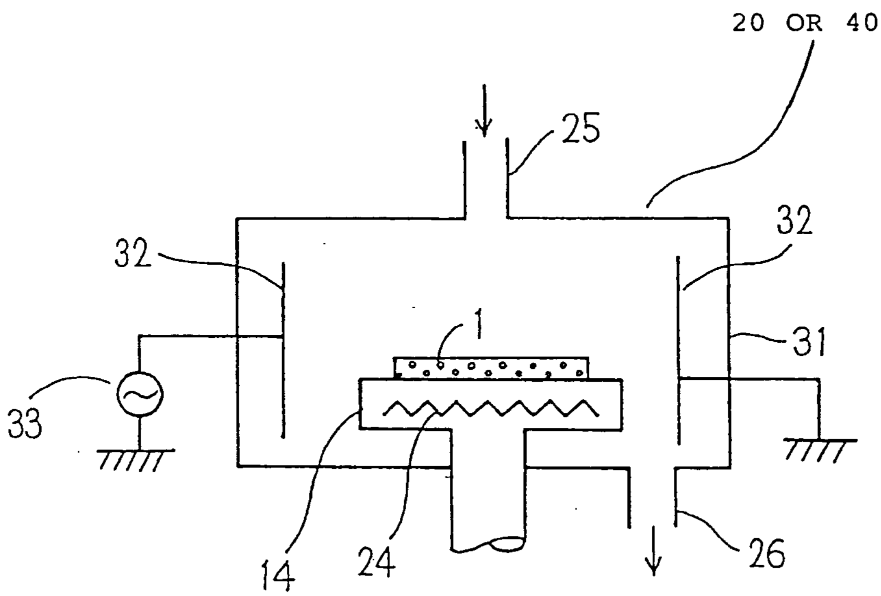
FIG. 5 (b)



F I G. 6



F I G. 7



F I G. 8

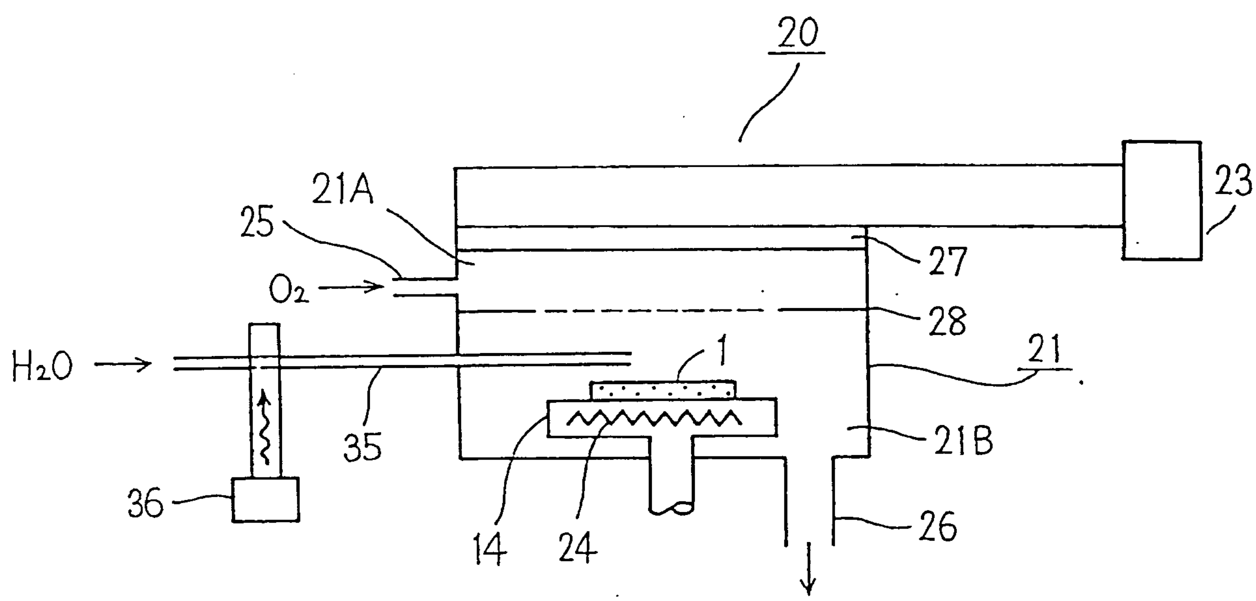
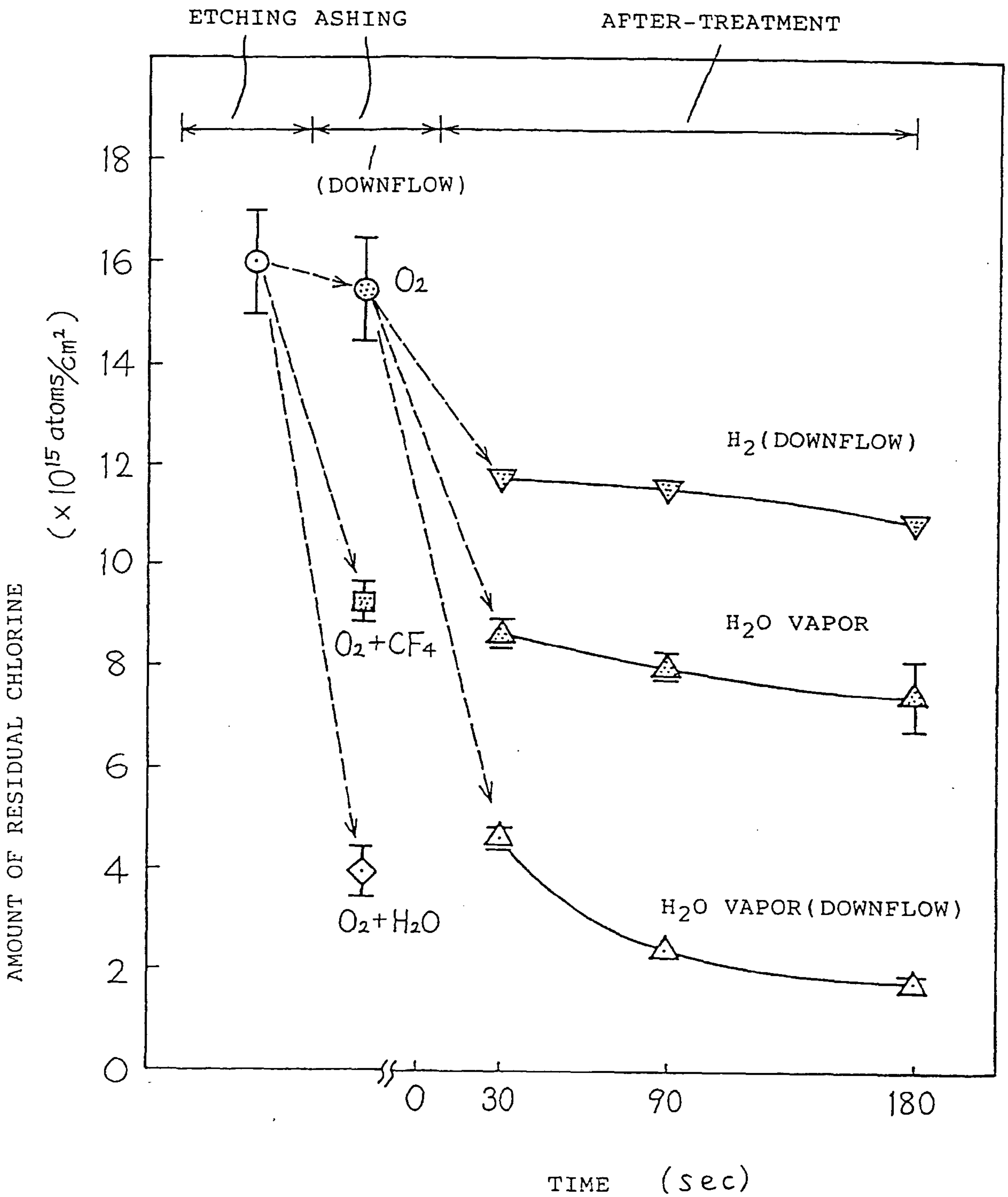


FIG. 9


ETCHING ASHING
AFTER-TREATMENT
(DOWNFLOW)
18
16
14
12
10
8
6
4
2
0
AMOUNT OF RESIDUAL CHLORINE
(× 10^{15} atoms/cm^2)
O_2
H_2(DOWNFLOW)
H_2O VAPOR
O_2+CF_4
H_2O VAPOR(DOWNFLOW)
O_2+H_2O
0
30
90
180
TIME (sec)

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00861

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 H01L21/302

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	H01L21/302, 21/027, G03F7/42

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1926 - 1991
Kokai Jitsuyo Shinan Koho	1971 - 1991

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 64-48421 (Fujitsu Ltd.), February 22, 1989 (22. 02. 89), (Family: none)	1-6
Y	JP, A, 64-30225 (Fujitsu Ltd.), February 1, 1989 (01. 02. 89), (Family: none)	1-6
A	JP, A, 1-239,933 (Tokyo Electron K.K.), September 25, 1989 (25. 09. 89)	1-22
A	JP, A, 2-144,525 (Toshiba Corp.), April 26, 1990 (26. 04. 90)	1-22
A	JP, A, 2-49,425 (Toshiba Corp.), February 19, 1990 (19. 02. 90), (Family: none)	1-22
A	JP, A, 2-71,519 (Toshiba Corp.), March 12, 1990 (12. 03. 90), (Family: none)	1-22

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
September 17, 1991 (17. 09. 91)	September 30, 1991 (30. 09. 91)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	

Form PCT/ISA/210 (second sheet) (January 1985)

International Application No. PCT/JP91/00861

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	JP, A, 61-147,530 (Toshiba Corp.), July 5, 1986 (05. 07. 86), (Family: none)	1-22
A	JP, A, 2-72,620 (Nichiden Anelba K.K.), March 12, 1990 (12. 03. 90), (Family: none)	1-22

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers , because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims.

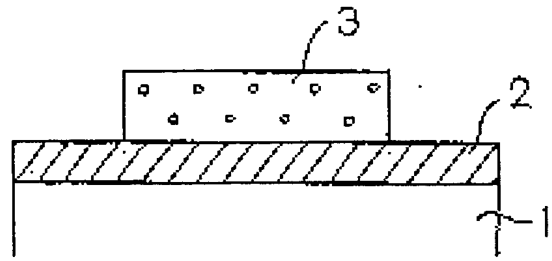
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee

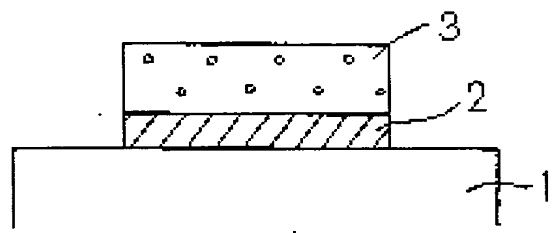
Remark on Protest

☐ The additional search fees were accompanied by applicant's protest

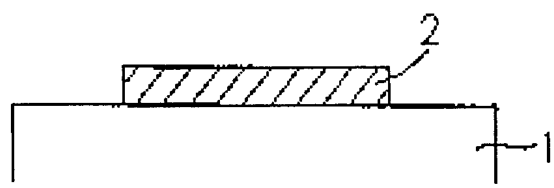
☐ No protest accompanied the payment of additional search fees.



F I G. 1 (a)

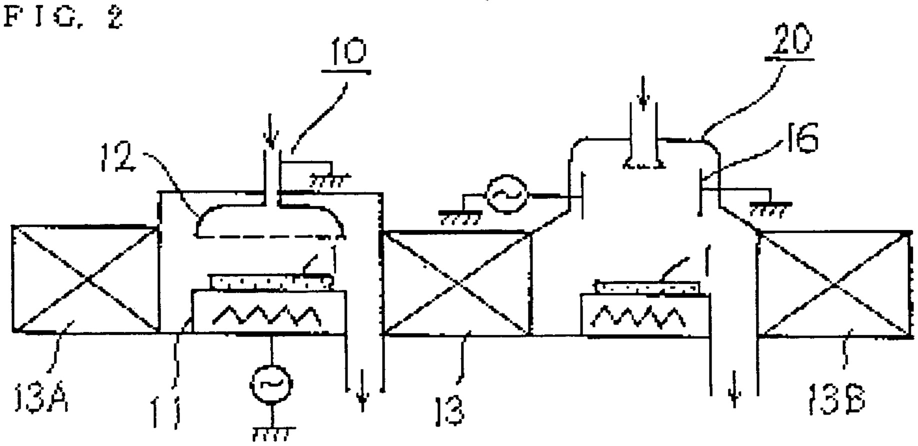


F I G. 1 (b)



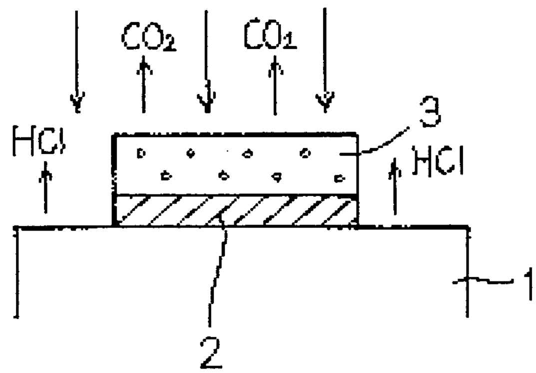
F I G. 1 (c)

F I G. 2



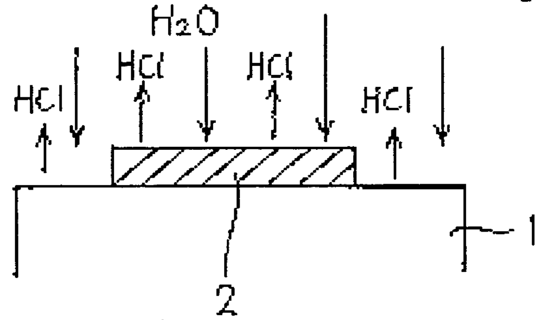
ACTIVE SPECIES OF O_2 AND H_2O

F I G. 3 (a)

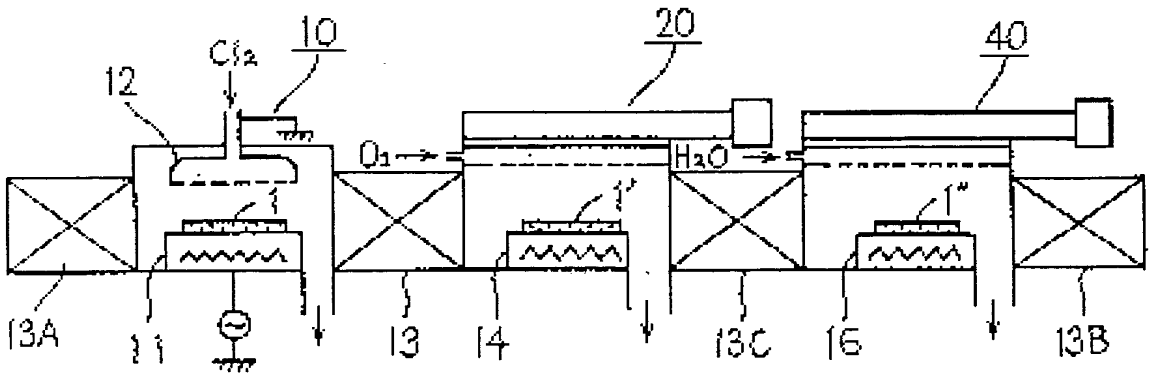


F I G. 3 (b)

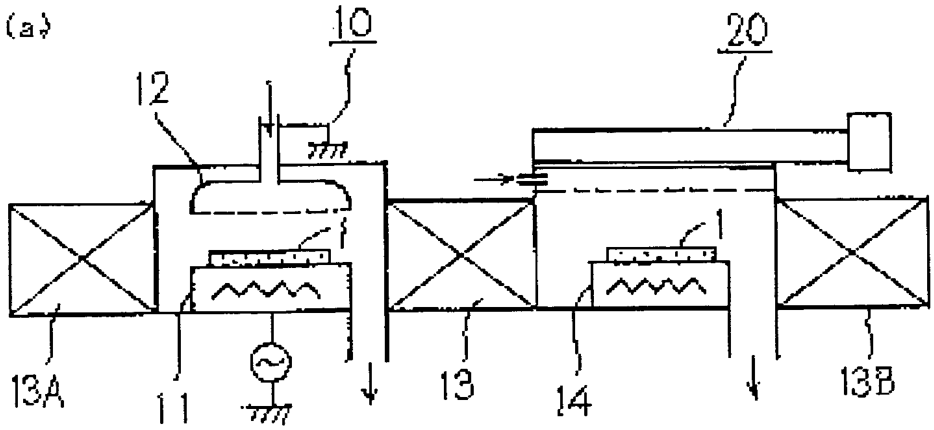
ACTIVE SPECIES OF H_2O



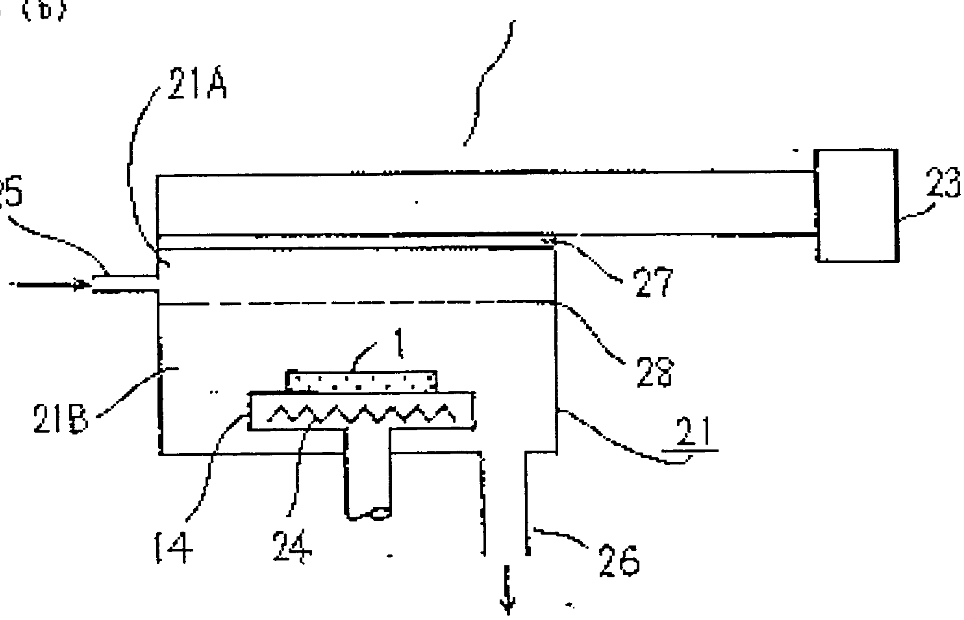
F I G. 4



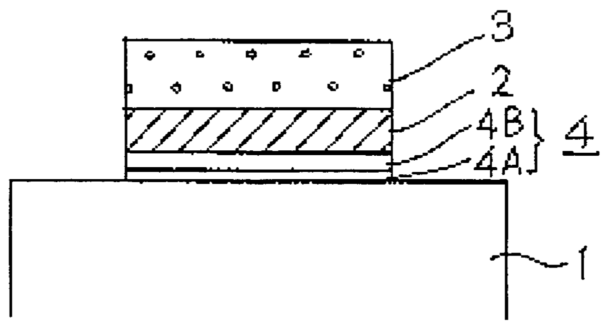
F I G. 5 (a)



F I G. 5 (b)



F I G. 6



F I G. 7

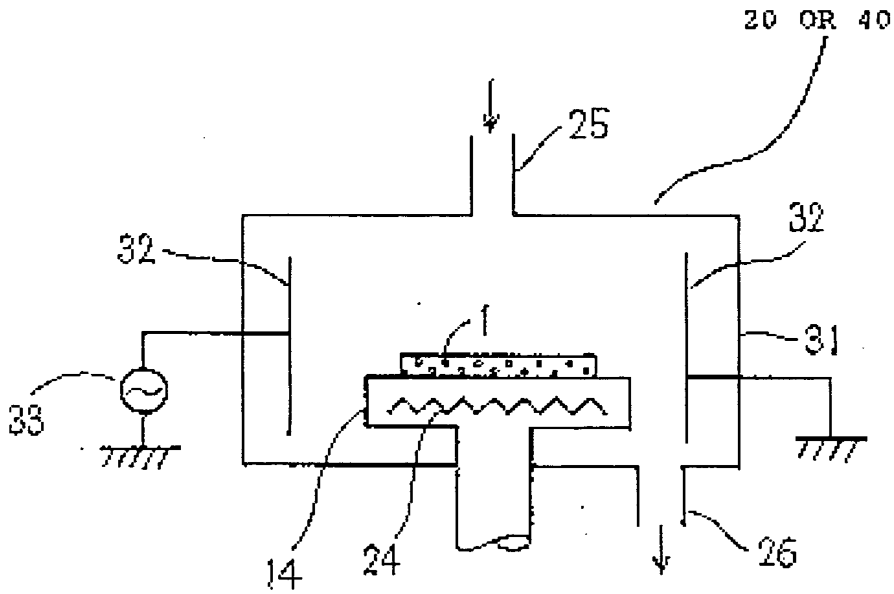


FIG. 8

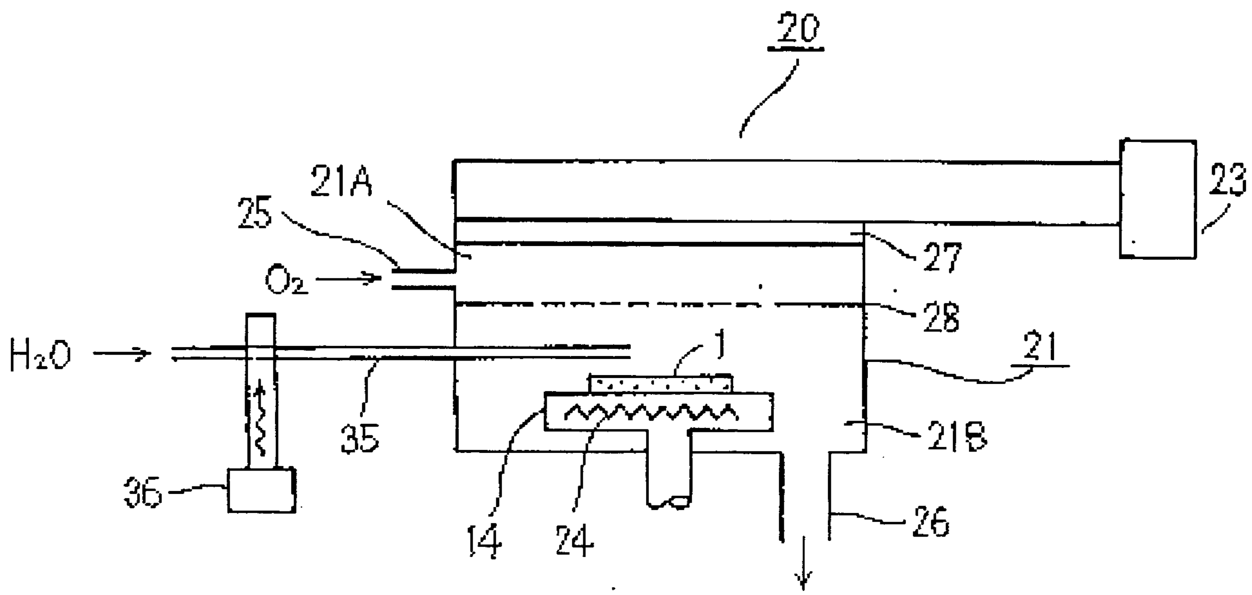
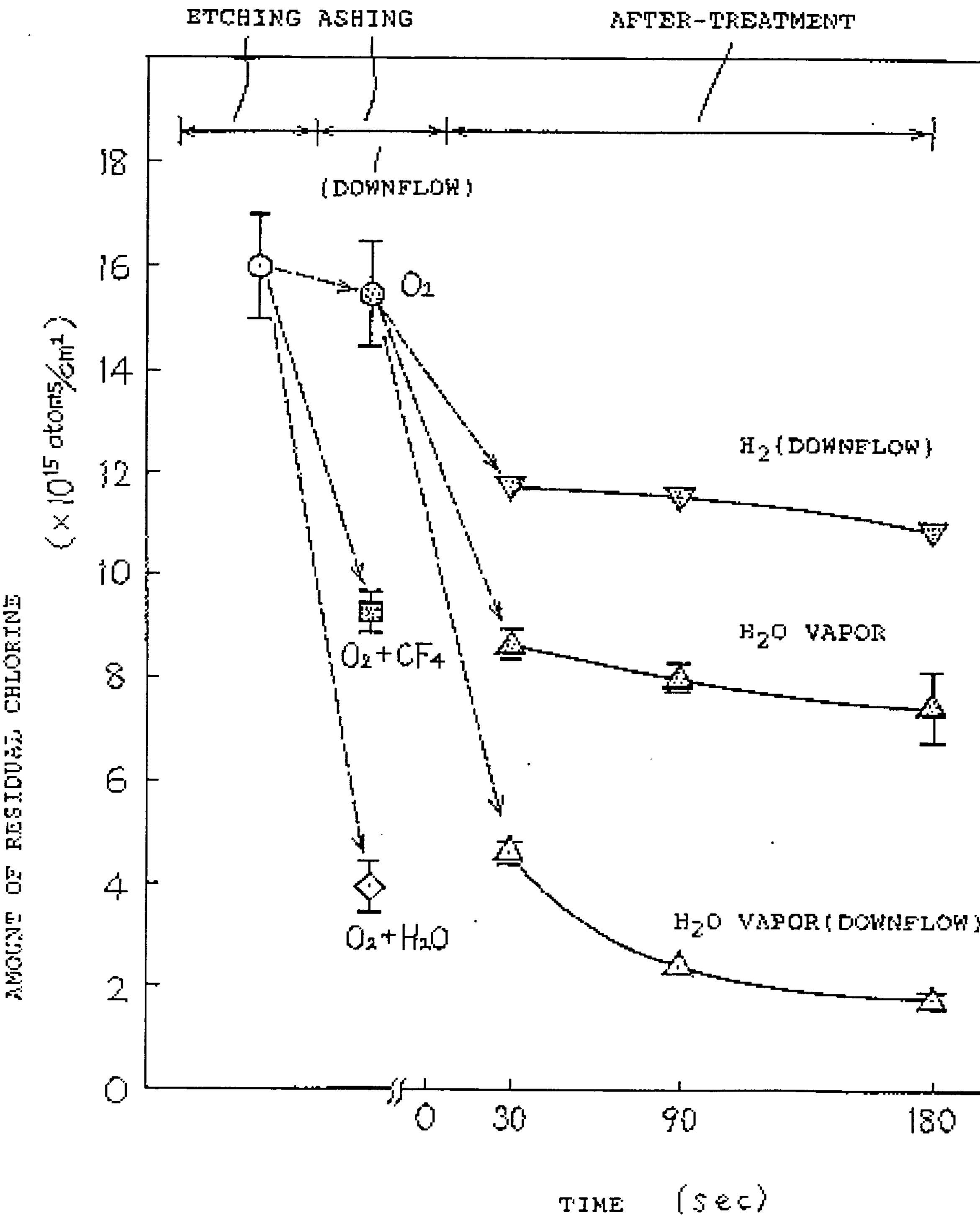


FIG. 9


ETCHING
ASHING
AFTER-TREATMENT
(DOWNFLOW)
AMOUNT OF RESIDUAL CHLORINE
($\times 10^{15}$ atoms/cm^2)
18
16
14
12
10
8
6
4
2
0
O_2
O_2+CF_4
O_2+H_2O
H_2 (DOWNFLOW)
H_2O VAPOR
H_2O VAPOR (DOWNFLOW)
0
30
90
180
TIME (sec)